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## **Towards Mechanochemistry of Fracture and Cohesion: General Introduction and the Simplest Model of Velcro**

**by Michael A. Grinfeld and Steven B. Segletes**

**ARL-TR-5309**

**September 2010**

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# **Army Research Laboratory**

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Weapons and Materials Research Directorate, ARL

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## 1. Novel Possibilities for Application of Mechanochemistry

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There are several reasons for this project. An acquaintance with any of the annual reviews of the U.S. Army Research Laboratory (ARL) (see, for instance, reference 1) or almost any issue of the Advanced Materials and Processes Technology Information Analysis Center (AMPTIAC) (see for instance, references 2–5 shows that numerous directions of research at the ARL are associated with consideration of mechanochemical systems). Among those are fracture of solids, analysis of solid explosives, chemical reactions in solids, environmental stress corrosion and coating with protective layers, creating composites by adhesives, technologies of the micro-electro-mechanical systems (MEMS) mounting, growth of semiconductor thin films, development of autonomic electric batteries, modeling of soft and hard tissues, *etc.* In fact, a common thermodynamic background of the macro-analysis of all those systems was not widely recognized mostly because of the “barbarism of specialization” (6) (the unavoidable socio-scientific phenomenon akin to the “confusion of tongues at Babel”).

Let us give several examples. First of all, by the very nature of their profession, the Department of Defense (DoD) and Army researchers and practitioners deal a lot with fracture of solid structures. Fracture is nothing else but a conversion of the (macroscopic) elastic energy into the energy of the broken bonds, i.e., the “chemical” energy. Typically, the “chemical” energy of the bonds is not mentioned explicitly and remains hidden behind the generic term of “surface” energy. The approach based on macroscopic description of the chemical bonds and their inclusion into the variational (later thermodynamic) scheme of classical mechanics can be traced back to the Laplace model of surface tension in liquids. Later, the same approach was used by Gibbs (7). His use of a thermodynamic variational formalism allowed analysis of heterogeneous systems and the various physico-chemical transformations therein. Several decades later, Griffith (8) suggested applying a similar approach to the analysis of fracture. Further developments along these lines may be found among the publications of Mott (9), Frenkel’ (10), Barenblatt (11), Raizer (12), and in the comprehensive reviews on fracture in reference 13. Starting from 2000, similar ideas have received some attention at ARL (14, 15).

The ideas of general thermodynamics, and of the Gibbs approach, in particular, have been expanding to include chemical reaction. While not done by Gibbs (the main contribution is due to Ostwald, van Hoff, and Arrhenius), the main construct of this generalization is associated with the Gibbs Grand thermodynamic potential. This potential is often (and not always correctly)

mentioned as the Gibbs potential or chemical potential. In this very name, the fundamental link between the mechanics and chemistry is particularly obvious.

An important further step in joining chemistry and mechanics belongs to Bridgman. In the experiments of 1930s (see the monograph [16]), he noticed the phenomenon of the rapid growth of the rate of chemical reactions under the action of shear stresses. His studies and observations have been continued by the Russian group of Enikolopyan (17–19). It is well documented that sufficiently strong mechanical stresses are able to change the rates of chemical reactions by orders of magnitude.

The role of mechanochemistry in the thermodynamics of solid explosives is far too obvious to warrant dwelling on a more detailed discussion. We would, however, like to mention here the recent studies of triggering hot spots in solid explosives—a project in the stage of rapid further development (20, 21).

The problem of coatings include two aspects of mechanochemistry: adhesion and stress corrosion. A corresponding review of the DoD requirements can be found in several issues of the Advanced Materials Manufacturing & Testing Information Analysis Center (AMMTIAC) (3, 4). Related studies at the ARL are presented in references 22–25.

The important role of mechanochemistry in the problem of individual and stationary electric power supply becomes obvious from the fact that the electrostatic force between charges at small distance is capable of generating huge stresses. The review of various DoD related issues of power supplies can be found in reference 5.

The scope of applications of mechanochemistry is growing rapidly. The ideas of macroscopic thermodynamics and of the Gibbs paradigm have penetrated into nanotechnology including quantum dots and quantum wire growth, epitaxial growth of nano-scale films, *etc.* Another area of rapidly growing application of mechanochemistry is the biomechanics of tissue, including soft and bone tissue. For soft tissue, the mechanochemistry is associated with the mechanism of adhesion. For bone tissue, the applications of mechanochemistry are associated with the important and well-documented phenomenon of bone remodeling under load.

So, we are able to see that there are a plethora of promising applications of mechanochemistry. In Russia, there is a large organization called the Institute of Mechanochemistry of the Russian Academy of Science in Novosibirsk, which is responsible for several reviews on mechanochemistry (see, for instance, references 26, 27).

There are plenty of novel possibilities for DoD-related studies. The very term “mechanochemistry” is more and more often heard at ARL. To date, this term is associated with mechanical milling of solids and the making of micro- and nano- powders. But, in fact, the scope of applications of mechanochemistry for DoD researchers is much wider. At ARL, the analysis of adhesives on the nanoscale level is mostly based on molecular dynamics simulations and similar techniques. As with any other technique, those approaches have several limitations. It is obvious, however, that one approach to modeling is, mildly speaking, underrepresented at the ARL—the approach based on macroscopic thermodynamic methods. These methods are deeply developed in many other branches of science. They are, basically, bare-hands methods leading to deep penetration into the subject with minimal effort. They provide researchers with intuitively transparent models, simple formulas, and reliable numerical schemes for subsequent computer-based modeling (relying, generally, on finite-element and similar techniques). We would like to fill this currently existing gap at ARL. We hope that, as a result of this effort, a new direction of research at ARL will be seeded: the thermodynamic analysis of the adhesive systems.

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## **2. Current Theoretical Difficulties in the Thermodynamics of Heterogeneous Systems and Fracture**

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The second target of this project is quite different from the first one. It is connected with the current state-of-the-art of thermodynamic methods in the theory of phase transformations and fracture in solids. This state-of-the-art can be characterized by a single word: crisis. It might look surprising when somebody talks about crisis in the era when thousands of papers appear in the scientific journals every year. In those sometimes sophisticated and elaborate papers, it is claimed that theory is in remarkable harmony with the experiment. If so, is there any reason to talk about crisis? Yes, there is.

The crisis is in the *predictive* ability of the current thermodynamic theories of heterogeneous systems with solid phases. The oft-demonstrated agreement of the theory and experiment should not be exaggerated. It is basically achieved by pumping the models with sufficiently many parameters. As John von Neumann once paraphrased Cauchy: “With four parameters I can fit an elephant, and with five I can make him wiggle his trunk.” But try to make an unbiased prediction based on those allegedly universal theories. In doing so, one will find that those predictions do not have much in common with reality.

The problem is not only with the number of tuning parameters *per se*. More importantly, those parameters require permanent and essential adjustments even when dealing with very close experimental settings. Of course, this situation is intolerable. We heard many complaints from fracture theorists that, in its current stage, fracture models are not able to predict numerous phenomena. For example, they are not able to predict the curvilinear trajectories of the propagating cracks, among many other phenomena.

Many critical words have especially come from theories based on the Griffith energetic approach, initiated in the classical paper (8) and continued in numerous other studies (9–13). In the Griffith model, the release of the bonds' energy is fulfilled across a single surface, called a crack. The Griffith "growing-crack" model was developed in various directions and has become the basis of numerous applications, despite its essential shortcomings.

We can add one more example to those complaints. One of us (Michael Grinfeld), over a lengthy period of time, was involved in the development of the Gibbs paradigm of analysis of heterogeneous systems with phase transformations.<sup>1</sup> The methods developed in reference 28 allow one to explore not only the condition of equilibrium of heterogeneous systems but also their stability and, in particular, the morphological instabilities of phase interfaces. In addition to many useful results, the theory, developed in reference 28, leads also to multiple results that have nothing in common with physical reality. These methods are already used in several research areas at ARL. It is clear that the cases in which the theory outlined in reference 28 appears to be misleading should be explored and made transparent for ARL users.

The unsatisfactory state-of-the-art in the theories of phase transformations and fracture is the second reason of the current (and future) study. To make some progress in understanding the existing difficulties, we propose exploring the strong features and weaknesses of the energetic (thermodynamic) methods by making theoretical and experimental studies of macroscopic adhesive systems. Basically, we plan to explore the mechanisms of attachment-detachment of the macroscopic adhesive tapes similar to the widely available Velcro<sup>2</sup>-tapes.

We strongly believe that by dealing with the macroscopic adhesives we will have a better chance of understanding of adequateness of the current theories of fracture, phase transformations, crystal growth, *etc.* What are our reasons for such aspirations?

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<sup>1</sup>Griffith fracture theory is nothing more than the very special heterogeneous system "solid - vacuum".

<sup>2</sup>Velcro is a hook-and-loop fastener system, which is a registered trademark of Velcro Industries B.V. In this report, we use the lowercase term "velcro" to refer to generic hook-and-loop fasteners in the style of Velcro.

Our hopes are mostly based on the larger likelihood of experimental verification of the theoretical predictions. Many experiments with adhesives can be made with bare hands and naked eyes. Similar experiments for heterogeneous systems, undergoing phase transformations and fracture, for example, would require very sophisticated experimental skills and expensive equipment. We realize that many researchers will ask us: “Is there anything in common between adhesion, fracture, and phase transformations?” The answer is affirmative. From the standpoint of thermodynamics, all these systems include, as an essential feature, the energy exchange between two storages of the accumulated energy—the energy accumulated due to reversible elastic deformations and the “chemical” energy stored in the chemical bonds. It is for these reasons that the systems require almost identical thermodynamic methods.

Thermodynamic methods are essentially macroscopic by origin and nature. They appear in the analysis of macroscopic engineering systems. They have been reliably validated in numerous macroscopic experiments and observations. Naturally, researchers later applied those methods to the systems way beyond the area in which they had been originally validated. In particular, the approaches are widely used in “all” physics at the nano-, micro-, and macro- levels. It is typical these days for macro-language and macro-cartoons to be widely used in modeling even nano-systems. There is nothing wrong with that as long as we realize that, while some aspects of the nano-system are like those of their macroscopic counterparts, others are completely different in nature. This unavoidable duality is emphasized in the very name “Quantum Mechanics” of this prototypical discipline.

In our opinion, mechanochemistry shares similar methodological features with quantum mechanics in what concerns the above-mentioned duality.

The mechanical component of mechanochemistry encourages the usage of macroscopic methods, and of thermodynamics, in particular. The chemical component encourages us to think on the nano- and atomic levels and use discrete modeling. We can capitalize, however, on the experience of our predecessors, who long ago made progress extracting those macroscopic features of the chemical subsystems, which can be analyzed by means of macroscopic methods. As a result, there can presumably be found areas that permit analysis of mechanochemical systems by means of relatively simple thermodynamic methods. From a purely thermodynamic point of view, the central problem of mechanochemistry is the exchange of energy between the (long-range) elastic energy and the (short-range) energy accumulated in individual bonds.

Fortunately, such an approach to the analysis of the mechanochemistry of fracture has been developed by the Russian theorists (10–12) and has received worldwide attention. It was initiated

by Frenkel' (10) who revealed conceptual problems in the Griffith paradigm and suggested the approach to fixing them by adding a more elaborate model of the subsystem of chemical bonds. He noticed, for instance, that the Griffith theory does not give the answer to the key question of the origin and disappearance of micro-cracks. In Griffith theory, the influence of the chemical bonds is modeled by means of adding the surface energy term (as was earlier suggested by Laplace in his variational theory of capillarity). Frenkel' suggested not to limit the analysis with a single constant to describe the surface energy density but, rather, to include explicitly a model of the chemical bonds, described as a system of springs.

The Frenkel' spring-model of the chemical bond should not be taken too literally. Actually, it substitutes for various mechanisms like electrostatic, van der Waals, and other types of physical forces. But those more elaborate models of forces cannot be directly included in the thermodynamic scheme, whereas the spring model can.

In this project, we will develop further the approach of Frenkel' (10) and his followers (11, 12). In his original paper, Frenkel' modeled the solid with the help of a bending-plate model. His followers used the model of an isotropic, linear-elastic solid instead of a bending plate. From a technical point of view, this implies significant added complexity because of the transition from ordinary differential equations to partial differential equations. More complicated models obviously diminish the depth of research attainable from analytical methods. For instance, the problem of stability of the equilibrium configurations has not been resolved in the studies (8, 10–12). Being quite difficult in its present form, these models (8, 10–12) are not precise enough to address the issues of stability. It is because their “elasticity” component is based on the linear theory—and linear elasticity is known to give misleading results in what concerns the analysis of stability.

In view of the facts mentioned previously, we choose the following approach. First, we will limit ourselves to the models adequately described by ordinary differential equations. Second, we will take into account only the membrane energy of the adhesive tape. That will allow us to avoid any assumptions of linearity at the stage of formulating the problems. Certain simplifying assumptions will appear later, at the stage of mathematical solution of the equations. As a result, we will get two advantages. First, we will have full confidence of the chosen model, since no uncontrollable assumptions have been made. In other words, we are guaranteed that our model will be consistent from the standpoint of the basic principles of mechanics, physics, and thermodynamics. Secondly, we will consistently address the issue of stability of the equilibrium configurations. This is very important because instability is a qualitative feature, which, if it exists, can be easily detected.

In this first report, we dwell on the simplest problem, the analysis of which does not require even differential equations—elementary algebra is sufficient for our purposes.

### 3. Thermodynamic Model of Velcro

State-of-the-art in modeling adhesives can be found in monographs (29–31). More specific studies of Velcro are presented in references 32 and 33. In the 1990s, velcro-ceramic composites were developed by the U.S. Army and U.S. Air Force for the purpose of providing armor protection while maintaining flexibility of manufacture and assembly. The Velcro component of the composite tiles play two roles: (1) it provides the fastening capability and (2) it gives a degree of shock resistance essential for the survival of the brittle ceramic. An analysis of these tiles, in the current context, would require a two-dimensional (2-D) approach using partial differential equations and multi-dimensional calculus of variations. Such an analysis goes beyond the scope of this report, which is based on one-dimensional (1-D) analysis and elementary calculus.

Consider, instead, the system shown in figure 1. Velcro is attached to a rigid flat substrate. The velcro fabric is assumed to be an inextensible thread of length  $L$ . The thread is loaded by the weight  $mg$ . Let  $x_f$  and  $x_R$  be the coordinates of the left and right ends of the attached part of the velcro. We assume that the velcro has negligible resistance to bending. However, despite the fact that the velcro is modeled to contain no (long-range) elastic energy, it nonetheless carries a (short-range) energy of distributed chemical bonds between the velcro and its attached substrate.

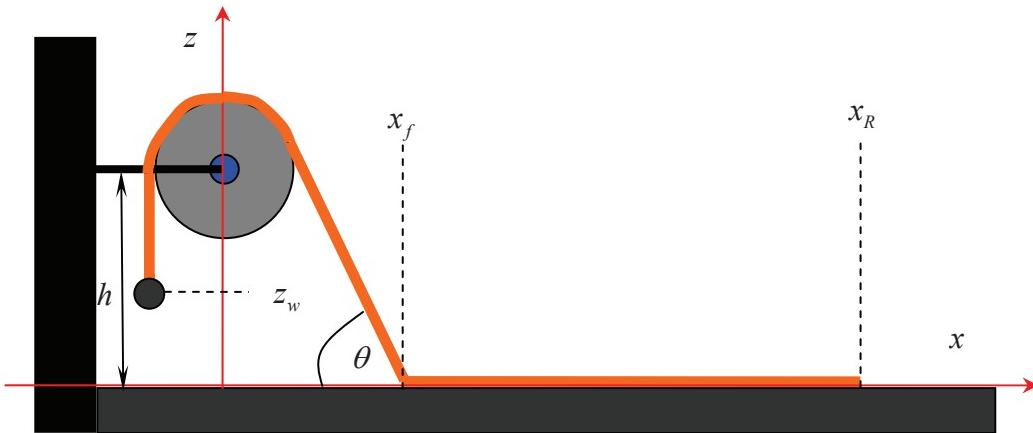


Figure 1. The simplest thermodynamic velcro model.

Let  $L_{\text{at}}$  be the length of an attached part of the velcro with the distributed chemical energy per unit length equal to  $\sigma_{\text{at}}$ , and  $L_{\text{de}} = L - L_{\text{at}} = L - x_R - x_f$  is the length of the detached part of the velcro with the distributed chemical energy per unit length equal to  $\sigma_{\text{de}}$ . Then, the total accumulated chemical energy  $E_{\text{chem}}$  is given by the formula

$$E_{\text{chem}} = \sigma_{\text{at}}L_{\text{at}} + \sigma_{\text{de}}L_{\text{de}} . \quad (1)$$

Neglecting the radius of the pulley, we obviously have the following geometric formula for the detached part of the thread:

$$L_{\text{de}} = h - z_w + \sqrt{h^2 + x_f^2} . \quad (2)$$

In addition to the accumulated chemical energy equation 1, the system also possesses gravitational energy  $E_{\text{grav}}$ . Thus, the total energy  $E_{\text{total}}$  of the system can be presented in the form

$$E_{\text{total}} = E_{\text{grav}} + E_{\text{chem}} = mgz_w + \sigma_{\text{at}}L_{\text{at}} + \sigma_{\text{de}}L_{\text{de}} \quad (3)$$

or, alternately, as

$$E_{\text{total}} = E_{\text{grav}} + E_{\text{chem}} = mgz_w + \sigma_{\text{de}}L_{\text{de}} + \sigma_{\text{at}}(x_R - x_f) . \quad (4)$$

In the presented model, the quantities  $\sigma_{\text{de}}$ ,  $\sigma_{\text{at}}$ ,  $g$ ,  $x_R$ ,  $L$ , and  $h$  are fixed. In essence, the total energy  $E_{\text{total}}$  can be presented as a function of a single variable  $x_f$ :

$$E_{\text{total}} = E_{\text{total}}(x_f) = mg \left( \sqrt{h^2 + x_f^2} - x_f \right) + \sigma_{\text{eff}}x_f + C , \quad (5)$$

where

$$\sigma_{\text{eff}} = \sigma_{\text{de}} - \sigma_{\text{at}} \quad (6)$$

and  $C$  is a constant.

### 3.1 Derivation of Equations 5 and 6

Let us derive the key formulas of the analysis, namely equations 5 and 6. With the help of the relationship 2 we can rewrite the total energy in the form

$$E_{\text{total}} = mgz_w + \sigma_{\text{de}} \left( h - z_w + \sqrt{h^2 + x_f^2} \right) + \sigma_{\text{at}}(x_R - x_f) . \quad (7)$$

The coordinate  $z_w$  can be excluded from the expression of the total energy, equation 7, with the help of the geometric formula for the total length:

$$h - z_w + \sqrt{h^2 + x_f^2} + x_R - x_f = L \quad , \quad (8)$$

implying

$$z_w = h + \sqrt{h^2 + x_f^2} + x_R - x_f - L \quad . \quad (9)$$

Eliminating  $z_w$  between equations 7 and 9, we arrive at the expression 5; the constants  $\sigma_{\text{eff}}$  and  $C$  are given by the formulas

$$\begin{aligned} \sigma_{\text{eff}} &\equiv \sigma_{\text{de}} - \sigma_{\text{at}} \\ C &= mg(h + x_R - L) + \sigma_{\text{de}}L - (\sigma_{\text{de}} - \sigma_{\text{at}})x_R \end{aligned} \quad . \quad (10)$$


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#### 4. Conditions of Equilibrium of Inextensible Velcro

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The condition of equilibrium of the velcro with respect to the coordinate  $x_f$  of detachment can be found by equating to zero the first derivative of the function  $E_{\text{total}}(x_f)$ :

$$\frac{dE_{\text{total}}(x_f)}{dx_f} = mg \left( \frac{x_f}{\sqrt{h^2 + x_f^2}} - 1 \right) + \sigma_{\text{eff}} = 0 \quad . \quad (11)$$

In terms of the angle  $\theta$ , shown in the figure 1, the equation 11 can be rewritten as follows:

$$1 - \cos \theta = \frac{\sigma_{\text{eff}}}{mg} \quad . \quad (12)$$

We can also write equation 12 as follows:

$$\left| \sin \frac{\theta}{2} \right| = \sqrt{\frac{\sigma_{\text{eff}}}{2mg}} \quad . \quad (13)$$

In the system described, the loading of the velcro was made by gravity. In this very system, however, the force  $mg$  could obviously have been replaced by an equivalent tension  $T$  applied to

the velcro. Thus, it is reasonable to rewrite equation 13 as

$$\left| \sin \frac{\theta}{2} \right| = \sqrt{\frac{\sigma_{\text{eff}}}{2T}} . \quad (14)$$

So far, we have established formula 14 for the case of gravitational loading only. It is rather appealing to assume, though, that formula 14 has much wider applications for different loading. This is not as obvious as one might think. In fact, the concept of force, and of tension, in particular, remains quite controversial. This is especially true when electro- and magnetostatic forces are taken into account. This is also true when the influence of the chemical bonding should be taken into account. For instance, the distinctions between the surface tension and the surface energy remain an issue of intense debate<sup>3</sup>.

The equation 14 is the central formula of the purely thermodynamic model of the velcro detachment and of this report. This formula shows that the angle  $\theta$  diminishes when the tension  $T$  grows. In particular, the angle approaches zero when the tension approaches infinity—this qualitative conclusion seems intuitively transparent. The quantitative validity of this formula requires, as always, experimental verification.

For the angle  $\theta = \pi/2$ , the formula 14 implies

$$\sigma_{\text{eff}} = mg . \quad (15)$$

Its physical meaning is absolutely transparent. At this very angle, the incremental detachment  $dx_f$ , causing the release the chemical energy  $dE_{\text{chem}} = (\sigma_{\text{de}} - \sigma_{\text{at}})dx_f$ , completely converts into the decrease of the load height  $-dz_f = dx_f$ , causing consumption of the gravitational potential  $dE_{\text{grav}} = -mg dz_f = mg dx_f$ . By equating these energy increments, we arrive at formula 15.

From the standpoint of the physical intuition, equation 15 is not transparent at all. It can be used, however, for the macroscopic interpretation and measurement of the microscopic (or, if one wishes, nanoscale) concept  $\sigma_{\text{eff}}$ .

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<sup>3</sup>From the conceptual standpoint, it is remarkable and instructive that in our thermodynamic analysis the concept of tension within the velcro was completely eliminated from the derivation of the key formulas 12 and 13. The readers can legitimately argue that instead of basing it on the concept of tension we based our analysis on the much more vague concept of *energy*. This is a valid criticism that requires immediate justification. Our justification is the following: the vagueness of the concept of force often implies logical, mathematical, and computational inconsistencies of the physical models. In this respect, the development of models based on the energy approach carries a huge advantage. Even outstanding researchers quite often confuse this logical advantage with the universality of the law of energy conservation. We will not dwell here on a more detailed discussion of this somewhat metaphysical issue.

The magnitude of  $\sigma_{\text{eff}} = \sigma_{\text{de}} - \sigma_{\text{at}}$  can, in fact, change in time due to various micro- and nanoscale phenomena like chemical contamination, absorption, desorption, environmental changes, *etc.* The result will be indicated by the macroscopic variation in the detachment length.

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## 5. Condition of Stability of Inextensible Velcro

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The issue of stability of the equilibrium configuration can be addressed by calculating the second derivative of the function  $E_{\text{total}}(x_f)$ . The direct calculation gives us

$$\frac{d^2 E_{\text{total}}(x_f)}{dx_f^2} = \frac{mg}{(h^2 + x_f^2)^{3/2}} . \quad (16)$$

According to equation 16, the second energy variation is always greater than zero. Thus, in the framework of thermodynamic theory, the equilibrium configuration is always stable.

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## 6. Extensible Velcro Model

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We can make one more important extension to the model without any necessity for considering ordinary or partial differential equations.

We now assume that the total internal energy  $E_i$  of the system consists of the distributed “elongation” energy  $E_{\text{el}}$ , accumulated in the detached part of the stretched thread, and the distributed “chemical” energy  $E_{\text{chem}}$  of the velcro bonds:

$$E_i = E_{\text{el}} + E_{\text{chem}} . \quad (17)$$

We assume that the attached part of the velcro cannot undergo any stretching. Let  $E_{\text{el}}$  be defined by the following relationship:

$$E_{\text{el}} = L_{\text{de}}^{\circ} e(\lambda) , \quad (18)$$

where  $L_{\text{de}}^{\circ}$  is the “reference” length of the detached part of the thread and  $\lambda$  is the elastic elongation of the thread.

The total chemical energy of the system is equal to

$$E_{\text{chem}} = \sigma_{\text{de}}(\lambda) L^{\circ} + \sigma_{\text{at}}(x_R - x_f) \quad (19)$$

where  $\sigma_{\text{de}}(\lambda)$  is a positive material function and  $\sigma_{\text{at}}$  is a positive material constant.

In this case, the total energy  $E_{\text{total}}^{\text{ext}}(x_f, \lambda)$  is given by an expression analogous to equation 5:

$$E_{\text{total}}^{\text{ext}}(x_f, \lambda) = mg \left[ \sqrt{h^2 + x_f^2} + (x_R - x_f - L^{\circ})\lambda \right] - [\sigma_{\text{de}}(\lambda) + e(\lambda)] (x_R - x_f - L^{\circ}) - \sigma_{\text{at}}x_f + C^*, \quad (20)$$

where  $L^{\circ}$  is the velcro's full unstretched "reference" length and

$$C^* \equiv \sigma_{\text{at}}x_R + mgh . \quad (21)$$

In the case when the surface energy  $\sigma_{\text{de}}$  of the detached film is independent of  $\lambda$ , the equation pair 20, 21 can be replaced with the following expression:

$$E_{\text{total}}^{\text{ext}}(x_f, \lambda) = mg \left[ \sqrt{h^2 + x_f^2} + (x_R - x_f - L^{\circ})\lambda \right] - (x_R - x_f - L^{\circ})e(\lambda) + (\sigma_{\text{de}} - \sigma_{\text{at}})x_f + C^{**}, \quad (22)$$

where

$$C^{**} \equiv -L^{\circ}\sigma_{\text{de}} + (\sigma_{\text{at}} - \sigma_{\text{de}})x_R + mgh . \quad (23)$$

## 6.1 Derivation of Equations 20 and 21

With the help of the relationships 17–19, we can rewrite the total energy in the form

$$E_{\text{total}}^{\text{ext}} = mgz_w + \sigma_{\text{de}}(\lambda) \frac{1}{\lambda} \left( h - z_w + \sqrt{h^2 + x_f^2} \right) + \sigma_{\text{at}}(x_R - x_f) \quad (24)$$

The coordinate  $z_w$  can be eliminated from the expression for the total energy, equation 7, with the help of the geometric formula of the total length:

$$\frac{1}{\lambda} \left( h - z_w + \sqrt{h^2 + x_f^2} \right) + x_R - x_f = L^{\circ} \quad (25)$$

implying

$$z_w = h + \sqrt{h^2 + x_f^2} + (x_R - x_f - L^{\circ})\lambda . \quad (26)$$

Eliminating  $z_w$  between equations 7 and 9, we arrive at the following chain of the relationships,

$$\begin{aligned}
E_{\text{total}}^{\text{ext}} &= mgz_w + \sigma_{\text{de}}(\lambda) \frac{1}{\lambda} \left( h - z_w + \sqrt{h^2 + x_f^2} \right) + \sigma_{\text{at}}(x_R - x_f) \\
&= \left[ mg - \sigma_{\text{de}}(\lambda) \frac{1}{\lambda} \right] z_w + \sigma_{\text{de}}(\lambda) \frac{1}{\lambda} \left( h + \sqrt{h^2 + x_f^2} \right) + \sigma_{\text{at}}(x_R - x_f) \\
&= \left[ mg - \sigma_{\text{de}}(\lambda) \frac{1}{\lambda} \right] \left[ h + \sqrt{h^2 + x_f^2} + (x_R - x_f - L^o) \lambda \right] + \\
&\quad \sigma_{\text{de}}(\lambda) \frac{1}{\lambda} \left( h + \sqrt{h^2 + x_f^2} \right) + \sigma_{\text{at}}(x_R - x_f) \\
&= mg \left[ h + \sqrt{h^2 + x_f^2} + (x_R - x_f - L^o) \lambda \right] - \\
&\quad \sigma_{\text{de}}(\lambda) \frac{1}{\lambda} \left[ h + \sqrt{h^2 + x_f^2} + (x_R - x_f - L^o) \lambda \right] + \\
&\quad \sigma_{\text{de}}(\lambda) \frac{1}{\lambda} \left( h + \sqrt{h^2 + x_f^2} \right) + \sigma_{\text{at}}(x_R - x_f) \\
&= mg \left[ \sqrt{h^2 + x_f^2} + (x_R - x_f - L^o) \lambda \right] - \sigma_{\text{de}}(\lambda)(x_R - x_f - L^o) - \\
&\quad \sigma_{\text{at}}x_f + \sigma_{\text{at}}x_R + mgh
\end{aligned}, \tag{27}$$

which will ultimately result in equations 20 and 21.

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## 7. Conditions of Equilibrium of Extensible Velcro

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Equating to zero the first derivative of the energy  $E_{\text{total}}^{\text{ext}}(x_f, \lambda)$ , we arrive at the following equations of equilibrium:

$$\frac{\partial E_{\text{total}}^{\text{ext}}(x_f, \lambda)}{\partial \lambda} = mg(x_R - x_f - L^o) - \left( \frac{d\sigma_{\text{de}}}{d\lambda} + \frac{de}{d\lambda} \right) (x_R - x_f - L^o) = 0 \tag{28}$$

and

$$\frac{\partial E_{\text{total}}^{\text{ext}}(x_f, \lambda)}{\partial x_f} = mg \left( \frac{x_f}{\sqrt{h^2 + x_f^2}} - \lambda \right) + \sigma_{\text{de}} - \sigma_{\text{at}} + e = 0 . \tag{29}$$

The force equilibrium condition 28 implies the relationship

$$\frac{de}{d\lambda} = mg - \frac{d\sigma_{\text{de}}}{d\lambda} . \tag{30}$$

Traditionally, the derivative  $de/d\lambda$  would be identified with the tension  $T$  of the extensible thread. Formula 30 indeed confirms this vision, provided that the surface tension  $\sigma_{de}$  is zero or that it is independent of the elongation  $\lambda$ . However, that is not the case. There is a nontrivial dependence on  $\sigma_{de}(\lambda)$ . It is wrong to think that such a dependence is somehow exotic. On the contrary, it is a typical situation in physical chemistry, and in mechanochemistry, in particular.

Let us turn now to the condition of chemical equilibrium 29. With the help of the condition of mechanical equilibrium 30, we can rewrite equation 29 as follows:

$$mg \left( \frac{x_f}{\sqrt{h^2 + x_f^2}} - \lambda \right) + \sigma_{de} - \sigma_{at} + e = 0 \quad (31)$$

or alternately as

$$\frac{d}{d\lambda} \frac{e + \sigma_{de} - \sigma_{at}}{\lambda} = 0 \quad . \quad (32)$$

Consider the model of extensible velcro described by the following conditions

$$\begin{aligned} \sigma_{de} &= \text{const.} \\ e &= \frac{K}{2}(\lambda - 1)^2 \end{aligned} \quad (33)$$

In this case, the equilibrium equations 30 and 31 provide the relationships

$$K(\lambda - 1) = mg \quad (34)$$

and

$$mg \left( \frac{x_f}{\sqrt{h^2 + x_f^2}} - \lambda \right) + \frac{K}{2}(\lambda - 1)^2 + \sigma_{de} - \sigma_{at} = 0 \quad . \quad (35)$$

With the help of equation 34, equation 35 can be rewritten as follows:

$$\lambda - \cos \theta = \frac{mg}{2K} + \frac{\sigma_{de} - \sigma_{at}}{mg} \quad , \quad (36)$$

which generalizes equation 12 and allows the calculation of the corrections for the finite magnitude of the elasticity module  $K$ .

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## 8. Condition of Stability of Extensible Velcro

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Calculating the second derivative of energy in vicinity of equilibrium configuration, we get

$$\begin{aligned}\frac{\partial^2 E_{\text{total}}^{\text{ext}}(x_f, \lambda)}{\partial \lambda^2} &= \frac{d^2(\sigma_{\text{de}} + e)}{d\lambda^2}(L^{\circ} - x_R + x_f) \\ \frac{\partial^2 E_{\text{total}}^{\text{ext}}(x_f, \lambda)}{\partial \lambda \partial x_f} &= 0 \\ \frac{\partial^2 E_{\text{total}}^{\text{ext}}(x_f, \lambda)}{\partial x_f^2} &= mg \frac{1}{(h^2 + x_f^2)^{3/2}}\end{aligned}. \quad (37)$$

In the case of constant surface energy density, equation 37 implies stability of the equilibrium configurations.

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## 9. Conclusion

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In this first report on the mechanochemistry of fracture and adhesion, we discussed possible applications of this discipline for the needs of Army researchers.

We formulated the simplest 1D model of a velcro-like adhesive and applied it to an analysis of equilibrium and stability, using an energy (variational) approach. The velcro was assumed to be partially attached to a rigid flat substrate. No assumption of small displacement of the velcro was made. For both the cases of inextensible and extensible velcro, the analysis appeared to be rather elementary and required only the standard techniques of multivariate calculus. No special knowledge of differential equations was required. We established the conditions of equilibrium for the system and proved that those configurations are always stable.

The model used here is a direct analogy of the Griffith crack model of brittle fracture. In the Griffith approach, the energy of the bond is modeled by introducing a constant called surface tension. The Griffith model was justly criticized by Iakov Frenkel' (10), who suggested a remedy based on introducing a finite zone of partial decohesion. This idea was further developed by many researchers, starting with the pioneering publications of Barenblatt *et al.* (11). In the zone of partial decohesion, the molecular interaction is modeled with extensible springs. One of our further goals will be to combine the model in this report with Frenkel's spring model.

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